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NMR Spectroscopy of Organolithium Compounds, Part XX[1]

^{6}Li,^{29}Si Shift Correlation: A New Tool for Structural Studies of Silylsubstituted Organolithium Compounds

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Abstract: A 2D-HMQC experiment has been performed for the first time to correlate ^{6}Li and ^{29}Si resonances using scalar ^{6}Li,^{29}Si coupling in dilithium 1,4-diyl-1,4-diphenyl-1,2,3,4-tetrakis(trimethylsilyl)butane, where $^2J(^6\text{Li},^{29}\text{Si})$ and $^3J(^6\text{Li},^{29}\text{Si})$ amount to 0.3 and 0.7 Hz, respectively.

Two-dimensional NMR shift correlations based on scalar spin-spin coupling belong to the most important tools in structural analysis and homo- as well as heteronuclear experiments for quite a number of different nuclei have been introduced.[2] In the area of organolithium compounds,[3] aside from the standard ^{1}H,^{1}H and ^{1}H,^{13}C experiments (COSY and HETCOR/COLOC or HMQC/HMBC, respectively),[2] homonuclear ^{6}Li,^{6}Li correlations based on COSY,[4] INADEQUATE,[5] and TOCSY[6] sequences were successful. In addition, heteronuclear correlations between ^{6}Li and ^{13}C or ^{1}H have been shown to provide important structural information about the aggregation of these systems in solution.[7]

In the present communication we describe a new application of the 2D-HMQC pulse sequence with the first heteronuclear shift correlation for the spin pair ^{6}Li,^{29}Si. Dilithium 1,4-diyl-1,4-diphenyl-1,2,3,4-tetrakis(trimethylsilyl)butane (^{6}Li enrichment > 98%, ^{29}Si natural abundance [4.9%]), described in the preceding communication, has an "internal" and "external" lithium cation (**1**, Fig. 1). Only the former, associated with the lithium signal at 0.37 ppm (rel. to ext. 0.1 M LiBr in THF) shows in the 1D ^{13}C and ^{29}Si NMR spectra, respectively, ^{13}C,^{6}Li coupling and small but detectable ^{6}Li,^{29}Si coupling constants of 0.3 Hz for the geminal [^2J(Li,1-Si)] and 0.7 Hz for the vicinal [^3J(Li,2-Si)] interactions.[8] The standard HMQC pulse sequence[9]

I (^{6}Li) 90°_x----------Δ----------|-------------180°_x------------|-FID (t_2)
S (^{29}Si) -------------------------90°_x------------t_1-------------90°_ϕ

with the phase cycle of the BRUKER software yielded the two-dimensional spectrum shown in Fig.1, where a delay $\Delta = 1/2J$ of 710 ms for the preparation of *anti*-phase magnetization was used. This value is optimized for the larger coupling but also allowed the detection of the geminal cross peak. The assignment of the ^{29}Si resonances was unequivocally achieved via a INEPT-HMQC ^{13}C,^{29}Si shift correlation experiment[10] based on $^1J(^{13}\text{C},^{29}\text{Si})$, since C-1 and C-2 are distinguished by their spin-spin coupling to ^{6}Li and ^{1}H, respectively. The measurements were performed on an unlocked 9.7 T superconducting magnet with a double tuned probehead under ^{1}H decoupling, using the X coil for the ^{29}Si pulses and the retuned deuterium lock coil as ^{6}Li channel. This simple procedure makes the experiment easily accessible and further successful applications to silylated

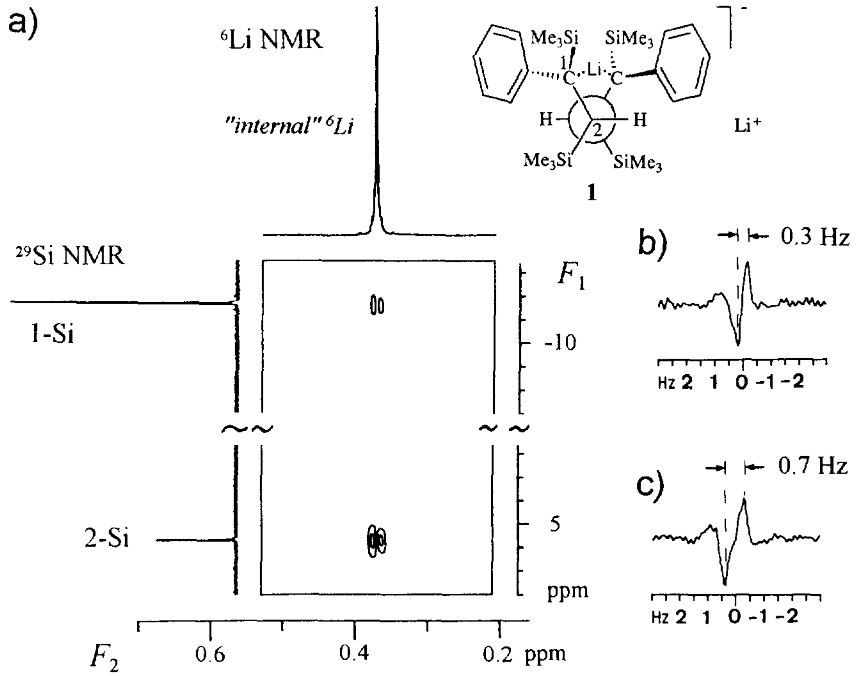

Fig. 1.a) 58.6/79.5 MHz ^{6}Li,^{29}Si shift correlation for **1** (0.7 M in [D$_8$]THF) measured on a BRUKER 400 MHz AMX spectrometer at 294 K; sweep widths F_1 (^{29}Si) 27.46 ppm (ref. TMS), F_2 (^{6}Li) 3.05 ppm (ref. ext. 0.1M LiBr in THF), 64 t_1 experiments, 2K data points in F_2; Δ delay 0.71 s, relaxation delay 3 s, acquisition time 5.71 s, total exp. time t_e 21.5 hrs; t_e is determined by the ^{6}Li relaxation time, the sweep width in F_2, and the number of t_1 increments and could be lowered to 8 hrs in other cases. b), c) traces through the cross peaks. The ^{6}Li signal at -1.20 ppm, not shown here, yields no cross peaks. It is assigned to the solvent separated "external" ^{6}Li cation.

dilithio compounds will be reported elsewhere.

References and Notes

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